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Promoter Effect on the Physico-Chemical Properties of Cobalt Based Catalyst for CO Hydrogenation

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Abstract

The effects of modification with promoters (Ru, Zr, Mn and K) on the properties of cobalt-based catalyst in CO hydrogenation were investigated by TPSR technique. The catalysts prepared by sol-gel method were characterized by BET, TPR and H_2-TPD. The effect of promoters was observed to have a profound impact on the physicochemical and catalytic properties of catalysts. Addition of Ru, K and Zr promoters to 30Co/MgO (30CM) facilitates the reducibility of catalyst. Mn addition improves the dispersion of metal clusters leading to a decrease in average cobalt crystallite size. Among all catalysts, 30Co-Mn/MgO (30CMM) and 30Co-Ru/MgO (30CRM) demonstrate the high reactivity and the maximum rate for methane formation. This could be attributed to the improvement of carbon monoxide chemisorption on high metal surface area of 30CMM and 30CRM catalyst. The change in physical and chemical properties of catalysts could be elaborated by the structural and electronic effects of promoter. Manganese effectively promotes cobalt supported magnesia catalyst by enhancement the C_{5+} selectivity.

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Keywords: Cobalt, CO hydrogenation, promoter, sol gel, TPSR

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1. Introduction

Fischer Tropsch synthesis (FTS) has been a topic of interest for production of liquid hydrocarbons from synthesis gas. Iron, cobalt, nickel and ruthenium have been commonly reported to be sufficiently active metal for Fischer Tropsch synthesis. Because of low cost compared to noble catalyst, iron and cobalt are practical catalyst for application in industrial scale, although they are active under high temperature or high pressure conditions to obtain desired products. Iron based catalysts are important for the formation of heavy hydrocarbon product with the desired olefin and oxygenate content and low CH_4 selectivity, whereas cobalt based catalysts predominantly present high activity and selectivity toward linear paraffin and low water-gas shift reaction [1-2]. For the production of liquid alkane hydrocarbons, cobalt catalysts are suitable for use in this purpose. The activity of cobalt for CO hydrogenation has been reported to depend on the support, preparation method, metal loading, dispersion and promoter [2]. One attempt to develop the catalyst performance in this research is the improvement of the catalytic activity and selectivity for FTS. Cobalt supported MgO catalyst was well prepared by modified sol gel technique and used as catalysts in this study. The effect of promoter Ru, Zr, Mn and K on the activity of cobalt based catalyst was investigated in CO hydrogenation by transient experiment using temperature programmed surface reaction technique (TPSR).

2. Methodology

2.1 Catalyst preparation

30%Co/MgO (30CM) catalyst was prepared by sol-gel method, using of $Mg(OC_2H_7)_3$. The solution was refluxed and stirred at 80-85 ^oC for about 2 h. Then, $Co(NO_3).6H_2O$ solution was added into the precursor solution. Portion of catalyst was dried and calcined in air at 400^oC.

30%Co-1%Ru/MgO (30CRM), 30%Co-1%Mn/MgO (30CMM), 30%Co-1%Zr/MgO (30CZM) and 30%Co-1%K/MgO (30CKM) catalyst were prepared in the same method using of $Mg(OC_2H_7)_3$. The solution was refluxed and stirred at 80-85 ^oC for about 2 h. Then, mixing solution $Co(NO_3).6H_2O$ and X (X; Ru, Mn, Zr and K promoter) was added into the precursor solution. Portion of catalyst was dried and calcined in air at 400^oC.

2.2 Catalyst characterization

The N_2 adsorption–desorption isotherms was measured by N_2 physisorption at -196^oC using a BELSORP-mini instrument. The surface areas (S_{BET}), pore volume and average pore diameter of catalysts were determined by the BET method (BELSORP-mini, BEL Japan Inc.). Sample was out gassed at 350^oC for 4 h before measurement.

The experiment of temperature programmed reduction (H_2-TPR) was carried out by using 0.20 g. catalyst packed in a tubular reactor. Catalysts were first flushed with Ar at 200^oC for 2 h and then cooled down to ambient temperature. Subsequently, the sample was heated to 800^oC at a heating rate of 10^oC/min under 5%H_2/Ar mixture at 30 mL/min. TCD signals were recorded from room temperature to 800^oC (Agilent 6820, USA).

Temperature programmed desorption (H_2-TPD) was performed after H_2 reduced and then cooled down to room temperature under the Ar atmosphere. Hydrogen was then chemisorbed on the catalyst for 30 min at ambient temperature, then flushed with Ar. The H_2-TPD profile was obtained by heating the sample to 800 ^oC at a rate of 10^oC/min under Ar flow. H_2 was detected by TCD detector (Agilent 6820, USA).

2.3 Hydrogenation of pre-adsorbed CO using TPSR technique

Temperature programmed surface reaction (TPSR) experiment was carried out in a fixed bed reactor using 0.200 g of catalyst. Before the TPSR was performed, a flow of 10%CO/He was allowed to the catalyst bed at room temperature for 30 min, following by flushing under He flow. TPSR experiment was studied under the condition of H_2 flow (30 mL/min). Temperature of catalyst surface was increased by temperature programmed from ambient temperature to 800°C with heating rate of 10°C/min. Methane product was detected by FID detector (Agilent GC 6820, USA).

2.4 Fischer-Tropsch reaction

The FTS reaction over the Co based catalyst was carried out in a fixed bed reactor (1.00 g of catalyst) at 200 °C, H_2:CO ratio of 2:1 at a flow rate of 80 mL/min for 24 h. Prior to the reaction, the catalyst was reduced by H_2 flowing at 750°C for 16 h . The effluent gas was analyzed by online gas chromatograph using TCD and FID (Bruker GC-450, USA). The liquid products collected in ice-bath cold trap were analyzed by an off-line GC (Bruker GC-430, USA) with FID.

3. Results and Discussion

3.1 Catalyst characterization

One important focus in the catalyst development of this research is the improvement of the catalytic activity by addition of promoters and employing modified sol–gel method for catalyst synthesis. The effect of promoter (Mn, Ru, K and Zr) on the physical properties of 30CM catalysts was observed. Promoter has an influence on the surface area of cobalt supported catalyst (Table 1). Comparison to the parent catalyst, Mn promoted catalyst shows the highest total surface area with the smallest average pore diameter, while K and Zr promoted catalyst present lower surface area with a similar average pore diameter to the parent catalyst. Ru and un-promoted catalyst give a similar total surface area. The addition of Mn effectively promotes the physical properties of catalyst in term of structural promoter by preventing the cobalt oxide particle agglomeration leading to the formation of small crystallites of cobalt oxide. Accordingly, 30CMM obviously presents high surface area. Other promoters especially K and Zr, presumably play a blocking effect on the catalyst surface resulting to a decrease in total surface area of catalyst.

%Dispersion, surface area of Co exposed and crystallite size of cobalt supported catalyst were investigated by H_2-TPD technique (Table 2). According to the results, it has to be mentioned that surface area of cobalt exposed decrease in the order of 30CMM >30CM > 30CRM > 30CZM > 30CKM. H_2-TPD results are obviously related to the results obtained from BET. High dispersion as well as high metal surface area of 30CMM could be explained by the formation of small crystallite size of catalyst in the presence of Mn promoter. Corresponding to Zhang et al. studied the Mn promotion in Co/Al_2O_3 catalysts [3]. It was found that the addition of Mn improves the dispersion of the active Co phase [4-5].

Table 1. Effect of promoter added on physical properties of 30CM catalysts.

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
30CM	87.25	0.59	27.18
30CRM	83.24	0.45	21.74
30CMM	110.09	0.49	17.87
30CZM	74.38	0.43	23.40
30CKM	49.26	0.34	27.81

Table 2. %Dispersion, surface area of Co exposed and crystallite size.

Catalyst	%Dispersion	Surface area of metal (m^2/g)	Crystallite size (nm)
30CM	6.65	44.97	14.99
30CRM	4.97	33.63	20.05
30CMM	7.83	52.97	12.73
30CZM	3.35	22.63	29.79
30CKM	2.24	15.15	44.49

Fig. 1. shows TPR profiles of Co catalysts with the addition of Ru, Mn, Zr and K. A difference in the reduction behavior was detected in the Co catalysts with and without metal promotion. The Co based catalysts undergo two typical steps during the reduction in the flow of H_2. The first step is attributed to the reduction of Co_3O_4 to CoO and the second step is assigned to the reduction of CoO to metallic cobalt [5-7]. The addition of Mn to the catalysts has slightly effect on the reducibility of cobalt supported magnesia catalyst. The reducibility and degree of reduction is similar to unpromoted catalyst. However, peak maximum at high temperature reduction slightly shifts to lower temperature indicating a beneficial effect on the reduction resulted by a decrease in cobalt support interaction promoting the reduction activity. For K, Ru and Zr promoted catalyst, TPR profiles obviously illustrate a shift of two partially overlapping peaks in a region between 200 and 450 ^oC, suggesting a significant increase in cobalt reducibility by electronic effect.

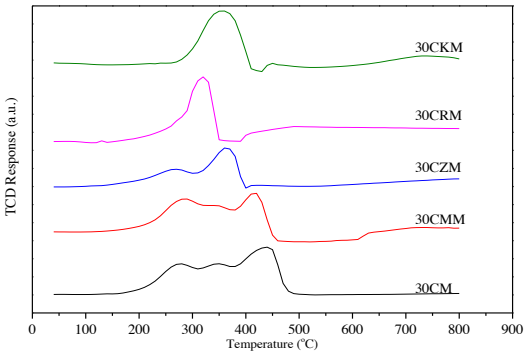


Fig. 1. TPR profiles of 30CM, 30CKM, 30CZM, 30CRM and 30CMM catalyst.

3.2 Hydrogenation of pre-adsorbed CO using TPSR technique

TPSR profiles obtained from the hydrogenation of pre-adsorbed CO over 30CM, 30CKM, 30CZM, 30CRM and 30CMM catalyst present in Fig. 2. The profile shows that the hydrogenation of pre-adsorbed CO leads to methane formation. TPSR results were summarized in Table 3. The initial temperatures for hydrogenation of pre-adsorbed CO drop according to the order of 30CM > 30CKM > 30CRM > 30CZM > 30CMM. The good result observed from 30CMM could be explained that the presence of Mn on the catalyst surface increases electron density on the cobalt active site, facilitating the CO chemisorptions. Zhang et al. studied the Mn promotion in Co/Al_2O_3 catalysts [3]. It was found that the addition of Mn favors the formation of bridge type adsorbed CO as probed with IR. This indicates a weakening of C-O bond and assisting its hydrogenation.

The amount of methane on different promoters decreases in the order of 30CMM >30CRM > 30CZM > 30CM > 30CKM. A higher of methane formation could indicate an increase in surface concentration of active Co metals. Although, the total surface area and dispersion of catalyst is not presented in the same trend, the actual metal surface area exposed is obviously more importance than the

total surface area and dispersion reported by BET and H_2-TPD. Peak temperature (T_{max}) shifts to lower temperature in the order of 30CM, 30CKM, 30CZM, 30CRM and 30CMM, respectively, suggesting an increase in the reactivity of catalyst.

Table 3. The Activation energies and amount of methane produced over all catalysts obtained from TPSR profiles.

Catalyst	Initial Temperature (°C)	T_{max} (°C)	Ea* (kJ/mole)	mol of CH_4/g catalyst
30CM	115	211	82.7	$9.53x10^{-5}$
30CKM	113	199	80.6	$8.49x10^{-5}$
30CRM	110	182	77.5	$1.29x10^{-4}$
30CZM	100	187	78.4	$1.15x10^{-4}$
30CMM	96	172	75.8	$1.39x10^{-4}$

*Activation energy is calculated by the following formula: = {Ea= R Tmax[ln(Ar Tmax [H2]/B)-3.9]} [8-9]

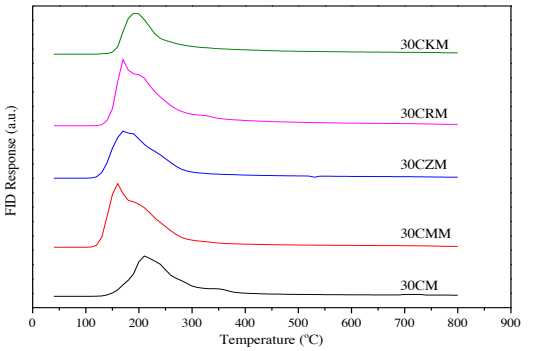
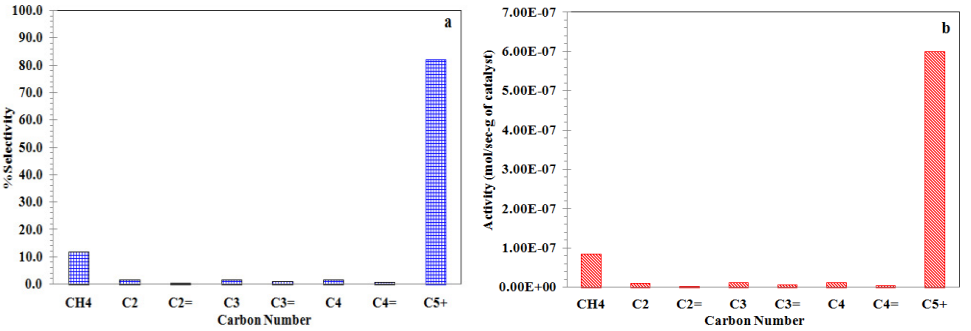


Fig. 2. TPSR profiles of 30CM, 30CKM, 30CZM, 30CRM and 30CMM catalysts.

3.3 Fischer-Tropsch reaction

From the characterization results, 30CMM catalyst exhibited excellent catalytic properties. Hence, 30CMM catalyst was chosen to test in the Fischer Tropsch reaction under the conditions of 200°C, H_2:CO ratio 2:1 and 1 bar. 30CMM catalyst shows the high C_{5+} selectivity (Fig. 3. (a)) and C_{5+} activity (Fig. 3. (b)). Hydrocarbon product distribution obtained from 30CMM catalyst also depicts the dominant curve of selectivity towards C_8–C_{13} fraction. (Fig. 3. (c))



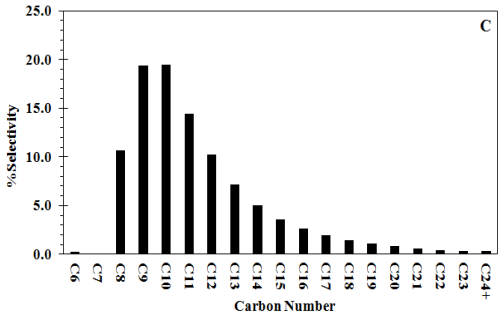


Fig. 3. %Selectivity (a) activity (b) liquid hydrocarbon product (c)

4. Conclusions

The effect of promoter Ru, Zr, Mn and K on the physicochemical and catalytic properties of Co/MgO catalyst for CO hydrogenation was studied in details. It could be concluded that the addition of Ru, Mn and Zr promoters can improve catalytic activity for CO hydrogenation. These findings suggest that Mn induces both structural and electronic promotion effects, resulting in higher metal dispersions and lower temperature for hydrogenation of CO activity of the catalyst as well as enhancement of the catalyst selectivity towards the long chain hydrocarbons (C_8–C_{13}) in Fischer Tropsch reaction.

Acknowledgments

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